Reviewer: John P. Knezovich, PhD
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Review of the Draft Report:
Water Quality Criteria for Cypermethrin
Phase III: Application of the pesticide water quality criteria methodology
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Overview
The freshwater criteria for cypermethrin cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate defined in this draft report was derived using methodology recently developed by Tenbrook *et al*. (2009)[1]. The methodology considers relevance of the endpoints and quality of the data in derivation of the criteria. This methodology was motivated by the California Regional Water Quality Control Board's desire to employ rigorous methods to develop criteria for protection of the Sacramento and San Joaquin River Watershed.

Basic information and physical-chemical data
The report provides a comprehensive summary of the physical-chemical data for cypermethrin. This data set is straightforward and indicates that this pesticide has low solubility, high density, low volatility, and high ability to bioaccumulate and sorb to organic material. Cypermethrin is moderately persistent in aqueous environments but is susceptible to rapid hydrolysis at basic pH. Overall, this pesticide's physical-chemical characteristics make its exposure to aquatic organisms a relevant concern.

Human and wildlife dietary values
The FDA has not set action levels for permethrin. Food tolerances for meat products should be reported in metric units (i.e., 50 µg/kg) and not ppm.

Avian mortality does not appear to be a concern for permethrin as the NOEC for mallard ducks is greater than 50 mg/kg. The last sentence in this section is poorly worded (i.e., "…it would be very unlikely to cause toxicity to birds ~~that~~ with significant food sources in water."). It appears that the intent of this statement is to indicate that cypermethrin concentrations in aquatic food items would not exceed 50 mg/kg. This conclusion is premature at this point in the report, as no data on cypermethrin concentrations in aquatic species has been presented.

Ecotoxicity data
The authors evaluated 108 published studies of cypermethrin toxicity to develop the proposed criteria (why is the number of studies qualified as "approximate"?). Relevance was determined using the aforementioned criteria[1] and data for studies that were deemed

[1] P. Tenbrook *et al*. (2009). *Methodology for derivation of pesticide water quality criteria for the protection of aquatic life in the Sacramento and San Joaquin River basins. Phase II: Methodology development and derivation of chloropyriphos criteria.* Report prepared for the Central Valley Regional Water Quality Control Board, Rancho Cordova, CA.

acceptable were evaluated. Adequate and reliable data is available for determining acute toxicity using animal studies and exclusion criteria appear to have been properly applied.

Data reduction
The rationale for the exclusion of chronic data presented in Table 7 requires clarification. The stated reasons for exclusion (i.e., less sensitive endpoint and less sensitive life-stage) do not appear to be appropriate for the test species (*Daphnia magna*), which was highly sensitive (as evidenced by the low LOECs) to cypermethrin in these tests. The fact that these tests were conducted as static renewals and not flow-throughs would appear to be a valid reason.

Acute criterion calculation
The acute criterion for cypermethrin was calculated using methods defined by Tenbrook *et al*. (2009). The five taxa required for the species sensitivity distribution (SSD) were available and the species sensitivity distribution (SSD) method was used. The Burr Type III SSD method was used to derive the median 5^{th} and 1^{st} percentile values. However, a log-logistic distribution method was used in favor of the Burr III distribution as the former provided a satisfactory fit to the data. Calculations using both methods appear to have been performed correctly. An acute criterion of 6 ng/L was recommended using the log-logistic distribution and the median 5^{th} percentile value and in accordance with Tenbrook et al. (2009).

Chronic criterion calculation
The acute-to-chronic ratio (ACR) method was used to derive the chronic criterion. The species mean ACRs span a range greater than two orders of magnitude (i.e., 2.11 – 949). The choice to use the SMACR for *Daphnia magna* (i.e., 949) was based on it being the only value within a factor of 10 of the acute 5^{th} percentile. Because the data for *D. magna* was derived from a study that did not use measured concentrations of cypermetrhin, this data is marginally reliable. The authors' correctly describe the issues with this study and are limited by the lack of other chronic data for daphnids.

Chronic criteria were calculated using both the recommended SMACR (949) and an "example" derived from the other two values (2.11 and 2.26) plus a default value of 12.4. As one would expect, these values result in significantly different criteria (0.01- and 3-ng/l). The authors recommend the lower value based on application of the Tenbrook *et al.* (2009) methodology. While this approach provides a conservative value for the chronic criterion, the weakness of the underlying data provides a cause for concern.

Bioavailabilty
Cypermethrin has a relatively high log K_{ow} value and therefore has a high tendency to sorb to dissolved and particulate organic materials. Due to their similar hydrophobicity, the bioavailability of cypermethrin is very similar to that of permethrin. The authors correctly point out that although ingestion of contaminated particles and food sources is likely an important route of exposure, it is not possible at this time to incorporate this pathway into criteria due to the lack of sufficient quantitative studies. Using the

dissolved phase of cypermethrin to assess compliance is appropriate and will require site-specific data on water characteristics.

Isolation of the dissolved phase of cypermetrhin by solid-phase micro-extraction presents a practical approach for approximating the bioavailable phase of this compound. Determination of site-specific dissolved concentrations of cypermethrin may not be practical, however, due to the need for accurate measurements of dissolved organic compounds and suspended solids, which require significant effort to acquire. The fact that these parameters can vary spatially and temporally further complicates such assessments and should be mentioned here. The authors cite the work of Bondarenko and Gan (2009), who reported a detection limit of 2.0 ng/L for cypermethrin. It is stated that this limit is below the acute criterion and is identical to the chronic criterion. However, the chronic criterion is 0.03 ng/L, which is well below the method limit of detection. The authors need to acknowledge this analytical shortfall and address its implications for criteria enforcement.

Mixtures
Additive and synergistic toxicity effects in the presence of other pesticides have been reported for cypermethrin. Because a variety of potential interactions are possible, it is not practical to apply a quantitative model to predict toxicity at this time.

Temperature, pH effects
An inverse relationship between pyrethroid toxicity and water temperature is well known. This relationship is important as laboratory toxicity tests are often conducted at temperatures that are higher than those in natural ecosystems. Although sufficient data does not exist to enable accurate predictions of temperature-related toxicity due to cypermethrin in aquatic ecosystems, this relationship should be considered in the derivation of safety factors as it is likely that criteria derived from laboratory studies conducted at relatively high temperatures will under-predict toxicity in many natural environments.

Data presented in Table 2 indicates that cypermethrin undergoes rapid hydrolysis at high pH. This needs to be mentioned in this section and implications for reduced risk in natural water bodies should be discussed.

Sensitive species
The derived acute criterion is reported here as 0.006 µg/L. It should be reported consistently as 6 ng/L. This criterion is higher that some reported acute toxicity values and may not be protective of all species. The authors acknowledge this and used the next lowest estimate from the species sensitivity distribution to drive an adjusted value of 1 ng/L based on the median 1st percentile value. While this is a conservative approach, it needs to be referenced (e.g., was it defined in the Tenbrook *et al*. methodology?). As presented, this approach seems somewhat arbitrary.

The development of the adjusted acute criterion causes a "trickle down" effect in the re-calculation of the chronic criterion, which has a new value of 0.003 ng/L. These calculations appear to have been performed correctly.

Ecosystem and other studies
The authors reviewed several studies that evaluated potential ecosystem impacts of cypermethrin in mesocosms and ecosystems. Impacts on invertebrates were only noted at concentrations of cypermethrin that exceeded the proposed acute and chronic criteria. No-observable effect levels were also higher than the proposed chronic criterion. The authors should note that many of these studies only reported nominal concentrations of cypermethrin and that actual dissolved concentrations were likely much lower than reported for these systems.

Threatened and endangered species
Fish (*Oncorhynchus spp.*) that are listed as endangered in California are represented in the data set that was used to derive the acute criterion. Because fish in general, and these species specifically, are relatively insensitive to cypermethrin, the proposed acute and chronic criteria should be protective of these species.

Data for other threatened or endangered species, including plants, were not in the data set and appropriate surrogates were not available. Accordingly, specific conclusions could not be offered for these species. However, the mode of action of cypermethrin indicates that it should not be highly toxic to plant species.

Bioaccumulation
Cypermethrin has a high K_{ow} and therefore a high potential to bioaccumulate in aquatic organisms. Reported bioconcentration factors are consistent with this K_{ow} and a bioaccumulation factor (BAF) approach was used to estimate the water concentration of cypermethrin that would result in a lethal concentration in wildlife that would consume contaminated fish. A definitive NOEC value for mallard ducks is not available and the single reported value of >50 mg/kg was used to calculate an aqueous NOEC. Using this approach, a water concentration of at least 6.0 µg/l would be required to produce a body burden of cypermethrin in fish that would be at the toxic threshold for mallards. This result clearly indicates that toxicity to mallards via food web transfer is unlikely. The high likelihood that such a water concentration, which exceeds the aqueous solubility of cypermethrin and would be acutely lethal to prey species, including fish, should be mentioned.

Harmonization with air and sediment criteria
Sediment and air quality standards for cypermethrin do not exist. However, because cypermethrin has a relatively high partition coefficient, dissolved concentrations may serve as a proxy for sediment burdens if Koc values are available for a given site. This is consistent with the previous discussion of bioavailability.

Limitations, assumptions, and uncertainties
Although there was sufficient data to derive the acute criterion, it is not clear why there was a lack of fit of the Burr III SSD. The authors suggest that more data points would lead to a satisfactory fit, but lack a basis for this conclusion. It is likely that the general lack of data form flow-through tests and reliance on nominal concentrations are significant contributors to the lack of consistency in the toxicity tests.

In the third paragraph of this section, the authors state that "nominal concentrations and static tests can underestimate the true exposure…". In fact, such factors will lead to an overestimation of exposure.

The chronic toxicity data set was limited by a lack of three of five required taxa and the lack of measured cypermethrin concentrations for key studies. The authors dealt with these shortcomings in a reasonable fashion; however, it does indicate that more and high quality data sets are required to develop more robust criteria.

The potential effect of lower temperatures on cypermethrin toxicity is potentially significant and should be considered in criterion development as more data becomes available.

Comparison to national standard methods
EPA (1985) methods were also used to attempt to derive acute and chronic criteria for cypermethrin. The EPA method faces the same limitation encountered in this report, that is, lack of data for all required taxa. Accordingly, neither acute nor chronic criteria could be calculated using EPA methods.

Final criteria statement
Derived using the best available data, the acute criterion of 1 ng/L and the chronic criterion of 0.003 ng/L should be protective of aquatic species in the Sacramento and San Joaquin River basins. The statement that the criteria were derived to be protective of aquatic life in the Sacramento and San Joaquin Rivers is a bit misleading, however, as the criteria were not derived exclusively using endemic species. The criteria were in fact derived for a generic freshwater North American ecosystem. The authors appropriately point out that the robustness of the derived criteria is limited by available data and should be updated as new information becomes available.